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DAVID W. TAYLOR NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

Bethesda, Md. 20084

Report MAT-75-20

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AN EVALUATION OF METHANOL, ETHANOL, THE PROPANOLS, AND THE BUTANOLS AS SHIP PROPULSION FUELS

by
Donald O. Newton

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An Evaluation of Methanol, Ethanol, the Propanols, and the Butanols as Ship Propulsion Fuels

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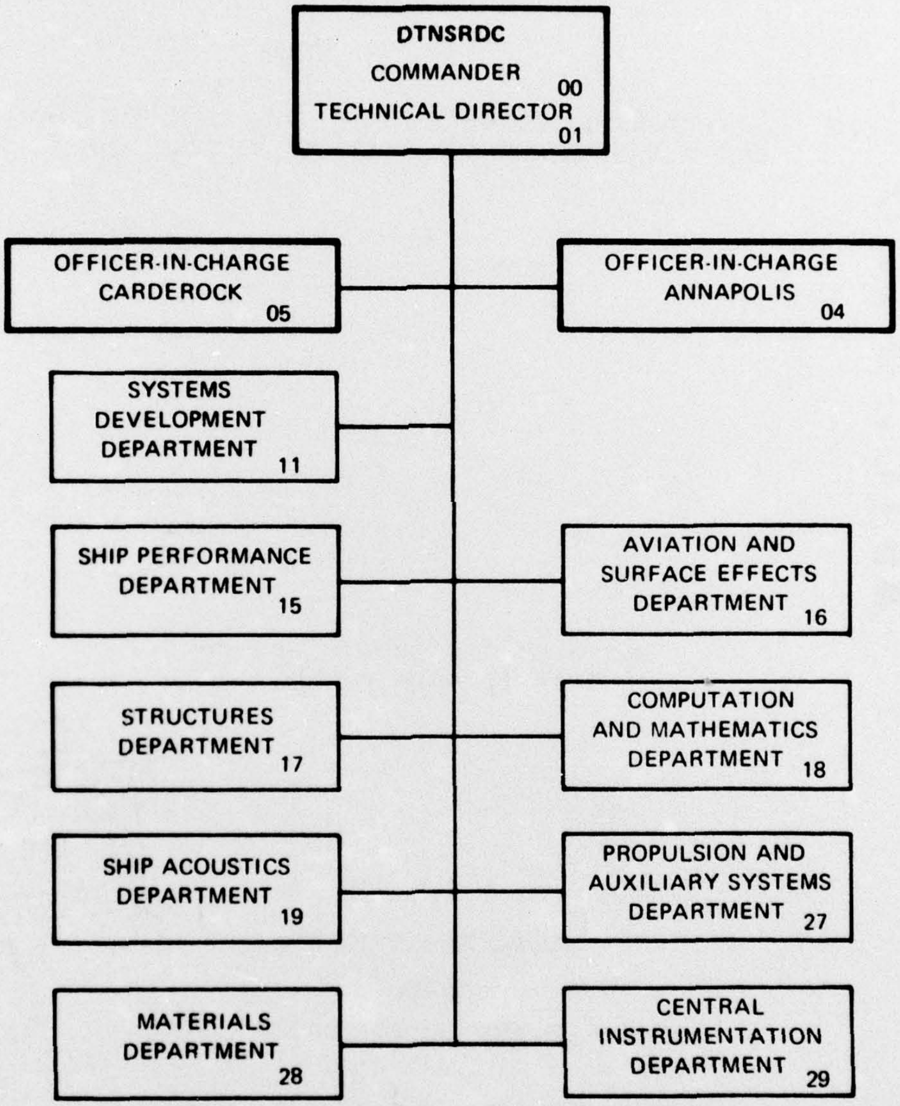

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This report evaluates the alkyl monohydric alcohols from methanol through the butanols (C-1 to C-4) as Navy ship propulsion fuels. Properties of the alcohols from the technical literature are compared with the properties of Navy ship propulsion hydrocarbon fuels (Diesel Fuel Marine and JP-5). None of these alcohols is suitable as a direct substitute or as an extender for

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the currently-used ship propulsion fuels. The use of methanol with its low volumetric energy content would entail over a 50% reduction in range between refuelings; the use of the other alcohols would result in roughly 25% to 40% loss of range. All the C-1 to C-4 alcohols have flash points below the 60° C minimum considered safe for shipboard fuels. Also, all have low cetane numbers, high water solubility, and problems with toxicity. However, methanol and mixtures of low-boiling alcohols are potentially usable as fuels for new ships specifically designed for their use.

(Author)

ADMINISTRATIVE INFORMATION

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ADMINISTRATIVE REFERENCES

(a) DTNSRDC Program Summary SF-57-571-301, Task 18306, Work Unit 2705-120 of 1 Aug 1976

(b) DTNSRDC Program Summary SSL 62001, Task 18310, Work Unit 2705-130 of 1 Aug 1976

LIST OF ABBREVIATIONS

° C	-	degrees Celsius
cSt	-	centistoke
DFM	-	*Diesel Fuel Marine, Mil Spec MIL-F-16884G*
° F	-	degrees Fahrenheit
GJ/m^3	-	gigajoules (10^9 joules) per cubie metre*
Hc	-	heat of cumbustion, lower net value
JP-5	-	jet fuel No. 5, Mil Spec MIL-P-5624G
p/m	-	parts per million
TLV	-	threshold limit value**

* GJ/m^3 x 3.59 = British Thermal Units per gallon.

** TLV has been defined to "represent conditions (in this case of vapor concentration) under which it is believed that nearly all workers may be repeatedly exposed day after day (8-hour) without adverse effect."

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ABSTRACT

This report evaluates the alkyl monohydric alcohols from methanol through the butanols (C-1 to C-4) as Navy ship propulsion fuels. Properties of the alcohols from the technical literature are compared with the properties of Navy ship propulsion hydrocarbon fuels (Diesel Fuel Marine and JP-5). None of these alcohols is suitable as a direct substitute or as an extender for the currently used ship propulsion fuels. The use of methanol with its low volumetric energy content would entail over a 50% reduction in range between refuelings; the use of the other alcohols would result in roughly 25% to 40% loss of range. All the C-1 to C-4 alcohols have flash points below the 60° C minimum considered safe for shipboard fuels. Also, all have low cetane numbers, high water solubility, and problems with toxicity. However, methanol and mixtures of low-boiling alcohols are potentially usable as fuels for new ships specifically designed for their use.

INTRODUCTION

When other sources of energy are considered[1] as alternates to the diminishing supply of domestic petroleum crude, "alcohol" is frequently suggested. To the layman the term alcohol usually means methanol (wood alcohol) or ethanol (grain alcohol). These are produced industrially in the largest volume and at the lowest cost. Isopropyl alcohol, a propanol, is familiar as the major ingredient of rubbing alcohol. It is also used as a solvent, as are the butanols and higher molecular weight alcohols, but these are less well known.

The use of methanol and ethanol as fuel is not new. Extensive investigation of their use as fuels for spark ignition internal combustion engines have been reported.[2-5] A good deal of effort was expended during the 1930's on the possible use of grain alcohol (ethanol), a product of surplus farm produce, either to replace gasoline or to be used in admixture with gasoline for automotive use.

With such a history it is not surprising that alcohol should again be suggested as a replacement for petroleum derived fuels, now that the nation has become aware of the decreasing availability of domestic petroleum. Neither is it unexpected to find "clean-burning alcohol" suggested as a potential substitue for the Navy's ship propulsion fuel

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[1]Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

DFM* and for JP-5 which is the current acceptable substitute for DFM. Consequently, a study has been made to determine whether the properties of the more important commercial monohydric alcohols are such that these alcohols would be suitable ship propulsion fuels in existing fuel systems, engines, and ships.

This report presents the results of that study. It lists a series of critical properties of the alcohols from methanol through the butanols and discusses the implications of those properties relative to the potential of their satisfactory use as ship propulsion fuel.

APPROACH

Properties of the alcohols are available in the technical literature, so there was no need to conduct experiments to determine these properties. Consequently, the approach used was to obtain the necessary data through a literature search, to assemble the collected data for each alcohol, to compare the data with the specification and actual properties of DFM and JP-5 fuels, and to interpret the data in terms of shipboard operational implications.

ALCOHOL PROPERTIES

GENERAL

Simple monohydric alcohols are compounds containing a hydroxyl group (OH) in place of one of the hydrogens of the corresponding saturated alkane hydrocarbon; e.g., the alcohol methanol is CH_3OH, whereas the hydrocarbon methane is CH_4. The three simplest alcohols (methanol, ethanol, and isopropanol) are produced in the largest volume and are currently the lowest in price.

The low molecular weight one to four carbon (C-1 to C-4) alcohols approach water in some of their chemical properties, but as the number of carbon atoms in the alcohol molecule increases the more nearly it resembles the hydrocarbons. Generally, alcohols of the same molecular weight (isomeric alcohols) vary to some extent in their properties, depending upon whether they are "primary," "secondary," or "tertiary" with respect to the carbon atom to which the hydroxyl is attached. These differences are more pronounced for the lower molecular weight alcohols than for the higher members of the

*Definitions of abbreviations used are given on page i.

series. Alcohols are more reactive chemically than hydrocarbons and vary widely in their solvency power, water solubility, volatility, boiling points, and toxicity.

The following tabulation summarizes properties [5-10] of the C-1 to C-4 monohydric alcohols of significance in evaluating them as ship propulsion fuels. Specification requirements and/or typical properties of DFM and JP-5 are also shown in this tabulation for comparison purposes. Examination of the table reveals that the alkyl monohydric alcohols through the butanols are water soluble and have flash points below the minimum 60° C (140° F) allowed for shipboard propulsion fuels. They also have low heats of combustion and low cetane numbers: furthermore, except for ethanol, they possess atmospheric vapor concentration TLV's that could result in shipboard toxicity problems.

PROPERTIES OF ALCOHOLS AND NAVY PROPULSION FUELS

Fuel	Boiling Point ° C	Melting Point ° C	Flash Point ° C	Viscosity, cSt at 38° C	Solubility % in H_2O	TLV p/m	Hc GJ/m^3	Cetane Number
Methanol	65	-144	11	0.6	Infinite	200	16.7	0
Ethanol	78	-117	13	1.1	Infinite	1000	21.2	15
n-Propanol	97	-126	22	1.7	Infinite	200	24.5	*
Isopropanol	82	-89	12	1.8	Infinite	400	23.9	15
n-Butanol	117	-90	29	2.2	8	50	26.2	*
sec-Butanol	99	-115	24	4.7	64	150	26.2	15
ter-Butanol	82	-25	11	*	Infinite	100	26.0	*
DFM	220-405	-7	60+	1.8-4.5	0.01	**	36.2	45+
JP-5	195-250	-50	60+	ca 2.5	0.01	**	35.1	ca 39

*Data unavailable.
**The American Conference of Government Industrial Hygienists formula for calculating the TLV of petroleum distillates does not apply to materials with midboiling points over 200° C.

METHANOL

Almost all methanol (originally known as wood alcohol because it was a product of the destructive distillation of hardwood) is now produced by the Methanol Synthesis[11] which yields impure methanol. It is "moderately toxic," so drinking it or suffering long exposure to high vapor concentration can lead to blindness or death. However, it is no more poisonous than many other industrial chemicals (including gasoline). The particularly important properties of methanol are its high water solubility, high volatility, low flash point, low viscosity, low cetane number, and its low volumetric heat of combustion (46% that of petroleum hydrocarbon DFM).

ETHANOL

Ethanol, grain or wine alcohol, has long been known as a product of fermentation. Now, however, industrial ethanol is synthesized from ethylene made from natural or refinery gases. Industrial ethanol is generally denatured to prevent its use as a beverage. Ethanol is highly water soluble, volatile, and intoxicating. It has a low flash point, viscosity, and cetane number, as well as a volumetric energy content of 59% that of hydrocarbon DFM.

THE PROPANOLS

There are two isomeric propanols. The branched chain isopropanol is more economical to produce by the usual alcohol synthesis process and less poisonous than the straight chain n-propanol. Isopropanol is synthesized from propylene derived from natural or refinery gases by processes similar to those for ethanol. Isopropanol has nearly the same water solubility, volatility, flash point, viscosity, and cetane number as the other two low-boiling alcohols and a toxicity similar to methanol. Its volumetric energy content is 66% that of petroleum hydrocarbon DFM. With the exception of its higher flash point and greater toxicity, n-propanol is similar to isopropanol.

THE BUTANOLS

There are no large production facilities solely for making the butanols or the other higher alcohols. They are produced as by-products of the syntheses of methanol, ethanol, and isopropanol. Because of water solvency, flash point, energy content, and toxicity the butanols will not be satisfactory for fuel use as replacements for the petroleum DFM or JP-5 fuels.

SIGNIFICANCE OF SHIP'S FUEL PROPERTIES

VOLUMETRIC HEAT OF COMBUSTION

The volumetric heat of combustion (sometimes referred to as the energy density) of a Navy ship's fuel is vitally important because it determines range, speed, and, therefore, military effectiveness.

The low energy density of methanol (46%) compared to hydrocarbon DFM means that a ship powered by gas turbine, diesel, or boiler engines would require approximately twice the fuel storage space or its range would be halved. In order to accomplish ships' missions without twice as many rejuelings, each ship would need at least twice the fuel capacity.

The other alcohols considered in this report would also provide substantially reduced operating ranges. For ethanol, the reduction would be to 3/5 (59%), for isopropanol to 2/3 (66%), and for the butanols to 3/4 (72%) the output of hydrocarbon DFM.

Use of these lower alcohols as extenders of hydrocarbon DFM would reduce the energy density of the resultant mixture to the extent that the alcohols were present.

SAFETY

Flash point and toxicity are the two most important factors which influence the safety of a fuel. Flash point controls the ship's fire safety, and toxicity affects the crew. Navy instructions[12] control the fire hazard by limiting the flash point of allowable fuels to 60° C (140° F) minimum. To control toxicity and ensure safety, all fuel materials are cleared by the Bureau of Medicine and Surgery so that special handling instructions are developed and ship compartment ventillation is employed.[13]

Methanol is a more serious fire hazard than either DFM or JP-5, but less of a fire hazard than gasoline. Methanol has a lower flash point and can more readily reach an explosive vapor concentration limit than either of the current ship propulsion fuels (DFM or JP-5). The allowable TLV for nontoxic vapor exposure is nearly the same as that for gasoline.

Ethanol, the propanols, and the butanols are nearly as great a fire hazard as methanol. Ethanol is decidedly less, and isopropanol is somewhat less of a vapor toxicity exposure risk than methanol; normal propanol and the butanols are roughly equal to methanol.

Use of the lower alcohols as extenders of hydrocarbon ship propulsion fuels would have an effect on the toxicity and flash point out of all proportion to their concentration because of their volatility. In particular, the flash point of a mixture is greatly influenced by the value of the lower flash point ingredient.

EQUIPMENT COMPATIBILITY

Equipment compatibility means the satisfactory performance of these alcohols in present ships using the present handling practices and equipment. Only after a period of operation on methanol or the other alcohols could all the difficulties and advantages that a ship might experience be identified. However, the following points are pertinent:

- According to Wolfe[10] diesel engines operate very poorly on methanol, ethanol, isopropanol, and sec-butanol because of their very low cetane numbers.

- Seawater or freshwater could not be used to ballast fuel tanks (the current practice) since water is soluble in all the lower alcohols.

- The low viscosity of methanol and ethanol could lead to pump lubrication and system leakage problems.

- Corrosion problems would follow from the greater reactivity of the alcohols.

SUMMARY

None of the C-1 to C-4 monohydric alcohols is suitable as a direct substitute in present ships for the currently used ship propulsion fuels (DFM and JP-5).

- Using these alcohols would impose as much as a 50% reduction in range and effectiveness on the present Fleet.

- The flash points of these alcohols are below the minimum 60° C acceptable for shipboard use and must be considered unsafe.

- Other than ethanol, which is intoxicating, the vapors of these alcohols are more toxic than present ship propulsion fuels.

- These alcohols are soluble in water; hence, could not be used in a water compensated fuel system or in a system where the same tank can be used either for fuel or seawater ballast.

The lower molecular weight alcohols (C-1 to C-4) would not be desirable extenders in DFM and JP-5 because of their effect on the volumetric heat of combustion, flash point, toxicity, and water solubility.

RECOMMENDATION

Further Navy consideration of the C-1 to C-4 alcohols as fuels should be limited to new Navy ships specifically designed for their use.

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